

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08G 18/28, C09D 175/04, C08G 18/62	A1	(11) International Publication Number: WO 00/55229 (43) International Publication Date: 21 September 2000 (21.09.00)
(21) International Application Number: PCT/US00/06963 (22) International Filing Date: 16 March 2000 (16.03.00) (30) Priority Data: 60/124,850 17 March 1999 (17.03.99) US 60/175,728 12 January 2000 (12.01.00) US (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): UHLIANUK, Peter, William [US/US]; 6440 Bordman Road, Romeo, MI 48065 (US). NAGATA, Isao [JP/US]; 3745 Horseshoe Drive, Troy, MI 48083 (US). QUASHIE, Sape, Kwesi [US/US]; 30060 Northgate Drive, Southfield, MI 48076 (US). CHUNG, Ding-Yu [US/US]; 2062 Hickory Leaf, Rochester Hills, MI 48309 (US). HAZAN, Isidor [US/US]; 29900 Franklin Road No. 164, Southfield, MI 48034 (US). (74) Agent: DESHMUKH, Sudhir, G.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, NZ, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HIGH SOLIDS ACID ETCH RESISTANT CLEAR COATING COMPOSITION (57) Abstract The present invention provides for an etch and mar resistant low VOC clear coating composition most suitable for use as a top clear coat in multi-layered OEM or refinish automotive coatings. The coating composition includes isocyanate, silane and melamine components. The isocyanate component includes an aliphatic polyisocyanate. The composition may be formulated as a two-pack or one-pack coating composition, wherein the isocyanate functionalities are blocked with a blocker such as a mono-alcohol.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

HIGH SOLIDS ACID ETCH RESISTANT CLEAR COATING**COMPOSITION****BACKGROUND OF THE INVENTION**

5 The present invention generally relates to high solids, low VOC (volatile organic component) coating compositions and more particularly to low VOC clear coating compositions suited for multi-layered coatings used in automotive OEM and refinish applications.

Basecoat-clearcoat systems have found wide acceptance in the automotive finishes market. Continuing effort has been directed to improve the overall appearance, the clarity of the topcoat, and the resistance to deterioration of these coating systems at ever-higher application solids levels. Further effort has also been directed to the development of coating compositions having low VOC. A continuing need still exists for clear coating formulations having an outstanding balance of performance characteristics after application, particularly gloss and distinctness of image (DOI) at high solids levels. Melamine/acrylic polyol crosslinked or melamine self-condensed coatings for example, may provide coatings having acceptable mar but such coatings have poor acid etch resistance and decreased appearance at higher solids levels. On the other hand, isocyanate/acrylic polyol based 2K urethane coatings generally provide acceptable acid-etch resistance but such coatings have poor mar resistance. Therefore, a need still exists for coatings that not only provide acceptable mar and acid-etch resistance but also high gloss and DOI at the lowest VOC possible.

One approach described by Ntsihlele and Pizzi in an article titled "Cross-Linked Coatings by Co-Reaction of Isocyanate-Methoxymethyl Melamine Systems" (Journal of Applied Polymer Science, Volume 55, Pages 153-161-1995) provides for reacting aromatic diisocyanate with methoxymethyl melamine. However, a need still exists for a high solids clear coating composition, which upon a long-term exposure to sunlight does not yellow or become brittle and provides high gloss and DOI.

30 **Statement of the Invention**

The present invention is directed to a clear coating composition comprising isocyanate, silane and melamine components wherein said isocyanate component comprises an aliphatic polyisocyanate having on an average 2 to 6 isocyanate functionalities.

35 The present invention is also directed to a method of producing a clear coating on a substrate comprising:

applying a layer of a clear coating composition comprising isocyanate, silane and melamine components wherein said isocyanate component

comprises an aliphatic polyisocyanate having on an average 2 to 6 isocyanate functionalities; and

curing said layer into said clear coating.

One of the advantages of the present invention is its low VOC, which
5 is below the current guidelines of Environment Protection Agency (EPA) of the United States.

Another advantage is the mar and etch resistance and hardness of the coating resulting from the coating composition of the present invention.

Yet another advantage is the clarity and high gloss of the coating
10 resulting from the coating composition of the present invention.

As used herein:

“Two-pack coating composition” means a thermoset coating composition comprising two components stored in separate containers. These containers are typically sealed to increase the shelf life of the components of the
15 coating composition. The components are mixed prior to use to form a pot mix. The pot mix has a limited pot life typically a few minutes (15 minutes to 45 minutes) to a few hours (4 hours to 6 hours). The pot mix is applied as a layer of desired thickness on a substrate surface, such as an autobody. After application, the layer is cured under ambient conditions or bake cured at elevated temperatures
20 to form a coating on the substrate surface having desired coating properties, such as high gloss, mar-resistance and resistance to environmental etching.

“One-pack coating composition” means a thermoset coating composition comprising two components that are stored in the same container. However, one component is blocked to prevent premature crosslinking. After the
25 application of the one-pack coating composition on a substrate, the layer is typically exposed to elevated temperatures to unmask the blocked component. Thereafter, the layer is bake-cured at elevated temperatures to form a coating on the substrate surface having desired coating properties, such as high gloss, mar-resistance and resistance to environmental etching.

“Low VOC coating composition” means a coating composition that includes in the range of from 0 to 0.472 kilogram of organic solvent per liter (4
30 pounds per gallon), preferably in the range of from 0.118 (1 pound per gallon) to 0.178 kilogram of organic solvent per liter (1.5 pounds per gallon) of the composition, as determined under the procedure provided in ASTM D3960.

“High solids composition” means a coating composition having a solid component in the range of from 65 to 100 percent and preferably greater
35 than 70 percent, all in weight percentages based on the total weight of the composition.

“Clear coating composition” means a clear coating composition that produces upon cure, a clear coating having DOI (distinctness of image) rating of more than 80 and 20° gloss rating of more than 80.

5 “GPC weight average molecular weight” and “GPC number average molecular weight” means a weight average molecular weight and a weight average molecular weight, respectively measured by utilizing gel permeation chromatography. A high performance liquid chromatograph (HPLC) supplied by Hewlett-Packard; Palo Alto, California was used. Unless stated otherwise, the liquid phase used was tetrahydrofuran and the standard was polymethyl
10 methacrylate.

“Polymer particle size” means the diameter of the polymer particles measured by using a Brookhaven Model BI-90 Particle Sizer supplied by Brookhaven Instruments Corporation, Holtsville, N.Y. The sizer employs a quasi-elastic light scattering technique to measure the size of the polymer particles. The
15 intensity of the scattering is a function of particle size. The diameter based on an intensity weighted average is used. This technique is described in Chapter 3, pages 48-61, entitled Uses and Abuses of Photon Correlation Spectroscopy in Particle Sizing by Weiner et al. 1987 edition of American Chemical Society Symposium series.

20 “Polymer solids” or “composition solids” means a polymer or composition in its dry state.

“Aliphatic” as employed herein includes aliphatic and cycloaliphatic materials.

25 “Crosslinkable” means that the individual components of an adduct contain functionalities which react within the composition of the invention to give a coating of good appearance, durability, hardness and mar resistance.

“Acid etch resistance” refers to the resistance provided by a coated surface against chemical etching action by the environment, such as for example acid rain.

30 “Mar resistance” refers to the resistance provided by coating to mechanical abrasions, such as, for example, the abrasion of a coated surface, such as an automotive body, that typically occurs during washing and cleaning of the coated surface.

Applicants have unexpectedly discovered that contrary to
35 conventional approaches used in typical thermoset coating compositions, i.e., those involving polymers and crosslinking components, a very viable route lies in a combination of what would traditionally be considered as crosslinking agents for producing a unique low VOC high solids clear coating composition that

produces coatings having superior coating properties, such as clarity, and mar and etch resistance. Applicants have further unexpectedly discovered that by including a silane component in a clear coating composition, the solids level can be further increased without sacrificing the etch and mar resistance, gloss, DOI, and other desired coating properties. It is believed that the silane component acts as a substitute for a solvent typically used in a coating composition and reacts upon cure to generate a stable and durable crosslinking structure. Thus, the viscosity of the resulting coating composition can be substantially lowered without sacrificing coating properties.

The clear coating composition includes isocyanate, silane and melamine components. The isocyanate component includes an aliphatic polyisocyanate having on an average 2 to 6, preferably 2.5 to 6 and more preferably 3 to 4 isocyanate functionalities. The coating composition includes in the range of from 35 percent to 70 percent, preferably in the range of from 40 percent to 60 percent, and most preferably in the range of 45 percent to 55 percent of the aliphatic polyisocyanate, the percentages being in weight percentages based on the total weight of composition solids.

Examples of suitable aliphatic polyisocyanates include aliphatic or cycloaliphatic di-, tri- or tetra-isocyanates, which may or may not be ethylenically unsaturated, such as 1,2-propylene diisocyanate, trimethylene diisocyanate, tetramethylene diisocyanate, 2,3-butylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, 2,2,4-trimethyl hexamethylene diisocyanate, 2,4,4-trimethyl hexamethylene diisocyanate, dodecamethylene diisocyanate, omega -dipropyl ether diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 4-methyl-1,3-diisocyanatocyclohexane, trans-vinylidene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 3,3'-dimethyl-dicyclohexylmethane 4,4'-diisocyanate, meta-tetramethylxylylene diisocyanate, polyisocyanates having isocyanurate structural units such as the isocyanurate of hexamethylene diisocyanate and isocyanurate of isophorone diisocyanate, the adduct of 2 molecules of a diisocyanate, such as hexamethylene diisocyanate, uretidiones of hexamethylene diisocyanate, uretidiones of isophorone diisocyanate or isophorone diisocyanate, and a diol such as ethylene glycol, the adduct of 3 molecules of hexamethylene diisocyanate and 1 molecule of water (available under the trademark Desmodur[®] N of Bayer Corporation, Pittsburgh, Pennsylvania).

Aromatic polyisocyanates are not suitable for use in the present invention as the clear coatings resulting therefrom are too light sensitive and tend

to yellow with age and crack upon long term exposure to sunlight. As a result such clear coatings are not durable.

If desired, the isocyanate functionalities of the polymeric isocyanate may be capped with a monomeric alcohol to prevent premature crosslinking in a one-pack composition. Some suitable monomeric alcohols include methanol, ethanol, propanol, butanol, isopropanol, isobutanol, hexanol, 2-ethylhexanol and cyclohexanol.

The melamine component of the coating composition includes suitable monomeric or polymeric melamines or a combination thereof. Alkoxy monomeric melamines are preferred. The coating composition includes in the range of from 10 percent to 40 percent, preferably in the range of from 15 percent to 35 percent, and most preferably in the range of from 20 percent to 30 percent of the melamine, the percentages being in weight percentages based on the total weight of composition solids.

In the context of the present invention, the term "alkoxy monomeric melamine" means a low molecular weight melamine which contains, on an average three or more methylol groups etherized with a C₁ to 5 monohydric alcohol such as methanol, n-butanol, or isobutanol per triazine nucleus, and has an average degree of condensation up to about 2 and preferably in the range of about 1.1 to about 1.8, and has a proportion of mononuclear species not less than about 50 percent by weight. The polymeric melamines have an average degree of condensation of more than 1.9

Some of such suitable monomeric melamines include highly alkylated melamines, such as methylated, butylated, isobutylated melamines and mixtures thereof. More particularly hexamethylol melamine, trimethylol melamine, partially methylated hexamethylol melamine, and pentamethoxymethyl melamine are preferred. Hexamethylol melamine and partially methylated hexamethylol melamine are more preferred and hexamethylol melamine is most preferred.

Many of these suitable monomeric melamines are supplied commercially. For example, Cytec Industries Inc., West Patterson, New Jersey supplies Cymel[®] 301 (degree of polymerization of 1.5, 95% methyl and 5% methylol), Cymel[®] 350 (degree of polymerization of 1.6, 84% methyl and 16% methylol), 303, 325, 327 and 370, which are all monomeric melamines. Suitable polymeric melamines include high amino (partially alkylated, -N, -H) melamine known as Resimene[™] BMP5503 (molecular weight 690, polydispersity of 1.98, 56% buytl, 44 % amino), which is supplied by Solutia Inc., St. Louis, Missouri, or Cymel[®] 1158 provided by Cytec Industries Inc., West Patterson, New Jersey.

Cytec Industries Inc. also supplies Cymel® 1130 @ 80 percent solids (degree of polymerization of 2.5), Cymel® 1133 (48% methyl, 4 % methylol and 48 % butyl), both of which are polymeric melamines.

5 The coating composition preferably includes one or more catalysts to enhance crosslinking of the components on curing. Generally, the coating composition includes in the range of from 0.1 percent to 5 percent, preferably in the range of from 0.1 to 2 percent, more preferably in the range of from 0.5 percent to 2 percent and most preferably in the range of from 0.5 percent to 1.2 percent of the catalyst, the percentages being in weight percentages based on the
10 total weight of composition solids.

Some of the suitable catalysts include the conventional acid catalysts, such as aromatic sulfonic acids, for example dodecylbenzene sulfonic acid, para-toluenesulfonic acid and dinonylnaphthalene sulfonic acid, all of which are either unblocked or blocked with an amine, such as dimethyl oxazolidine and 2-amino-
15 2-methyl-1-propanol, n,n-dimethylethanolamine or a combination thereof. Other acid catalysts that can be used are strong acids, such as phosphoric acids, more particularly phenyl acid phosphate, which may be unblocked or blocked with an amine.

In addition to the foregoing, the coating composition preferably
20 includes a small amount of one or more organo tin catalysts, such as dibutyl tin dilaurate, dibutyl tin diacetate, stannous octate, and dibutyl tin oxide. Dibutyl tin dilaurate is preferred. The amount of organo tin catalyst added generally ranges from 0.001 percent to 0.5 percent, preferably from 0.05 percent to 0.2 percent and more preferably from 0.1 percent to 0.15 percent, the percentages being in weight
25 percentages based on the total weight of composition solids.

These catalysts are preferably added to the melamine component.

The silane component of the coating composition generally includes a polymer provided with at least one reactive silane group. The coating composition includes in the range of from 5 percent to 45 percent, preferably in
30 the range of from 10 percent to 40 percent, and most preferably in the range of from 15 percent to 35 percent of the silane component, the percentages being in weight percentages based on the total weight of composition solids.

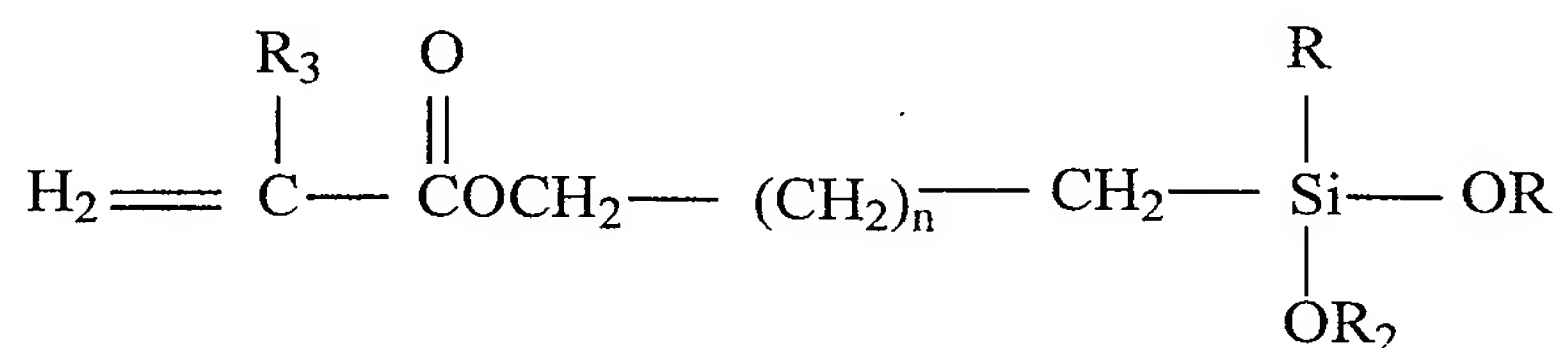
The silane polymers suitable for use in the present invention have weight average molecular weight in the range of about 100 to 30,000, preferably
35 in the range of about 120 to 25,000 and more preferably in the range of about 150 to 7,500. All molecular weights disclosed herein are determined by gel permeation chromatography using a polystyrene standard.

The silane polymer suitable herein is a polymerization product of about 30 to 95%, preferably 40 to 60%, by weight of ethylenically unsaturated non-silane containing monomers and about 5 to 70%, preferably 40 to 60%, by weight of ethylenically unsaturated silane containing monomers, based on the weight of the silane polymer. Suitable ethylenically unsaturated non-silane containing monomers are alkyl acrylates, alkyl methacrylates and any mixtures thereof, where the alkyl groups have 1 to 12 carbon atoms, preferably 3 to 8 carbon atoms.

Suitable alkyl methacrylate monomers used to form the silane polymer include methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, pentyl methacrylate, hexyl methacrylate, octyl methacrylate, nonyl methacrylate, and lauryl methacrylate. Similarly, suitable alkyl acrylate monomers include methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, pentyl acrylate, hexyl acrylate, octyl acrylate, nonyl acrylate, and lauryl acrylate. Cycloaliphatic methacrylates and acrylates also can be used, for example, such as trimethylcyclohexyl methacrylate, trimethylcyclohexyl acrylate, iso-butyl methacrylate, t-butyl cyclohexyl acrylate, or t-butyl cyclohexyl methacrylate. Aryl acrylate and aryl methacrylates, such as, for example, benzyl acrylate and benzyl methacrylate can be also used. It is understood that combinations of the foregoing monomers are also suitable.

In addition to alkyl acrylates or methacrylates, other polymerizable non-silane-containing monomers, up to about 50% by weight of the polymer, can be used in the silane polymer for the purpose of achieving the desired properties such as hardness, appearance, and mar resistance. Exemplary of such other monomers are styrene, methyl styrene, acrylamide, acrylonitrile and methacrylonitrile. Styrene may be used in the range of 0 to 50%, preferably 5% to 30% by weight of the silane polymer.

A suitable silane containing monomer useful in forming the silane polymer is an alkoxysilane having the following structural formula:

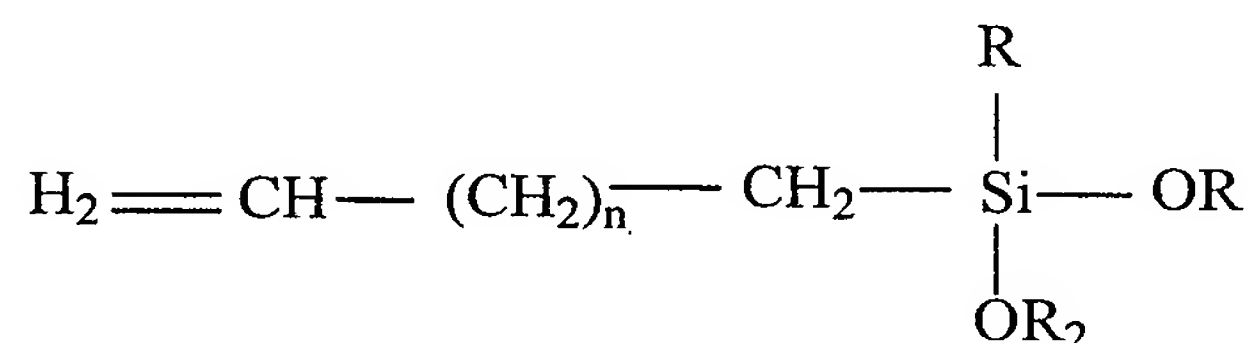


wherein R is either CH₃, CH₃CH₂, CH₃O, or CH₃CH₂O; R₁ and R₂ are CH₃ or CH₃CH₂; and R₃ is either H, CH₃, or CH₃CH₂; and n is 0 or a positive integer

from 1 to 10, preferably from 1 to 4. Preferably, R is CH₃O or CH₃CH₂O and n is 1.

Typical examples of such alkoxysilanes are the acrylatoalkoxy silanes, such as gamma-acryloxypropyltrimethoxy silane and the
5 methacrylatoalkoxy silanes, such as gamma-methacryloxypropyltrimethoxy silane, and gamma-methacryloxypropyltris(2-methoxyethoxy) silane.

Other suitable alkoxy silane monomers have the following structural formula:



10 wherein R, R₁ and R₂ are as described above and n is a positive integer from 1 to 10, preferably from 1 to 4. Examples of such alkoxysilanes are the vinylalkoxy silanes, such as vinyltrimethoxy silane, vinyltriethoxy silane and vinyltris(2-methoxyethoxy) silane.

Other suitable silane containing monomers are acyloxysilanes,
15 including acrylatoxy silane, methacrylatoxy silane and vinylacetoxysilanes, such as vinylmethyldiacetoxysilane, acrylatopropyltriacetoxysilane, and methacrylatopropyltriacetoxysilane. It is understood that combinations of the above-mentioned silane containing monomers are also suitable.

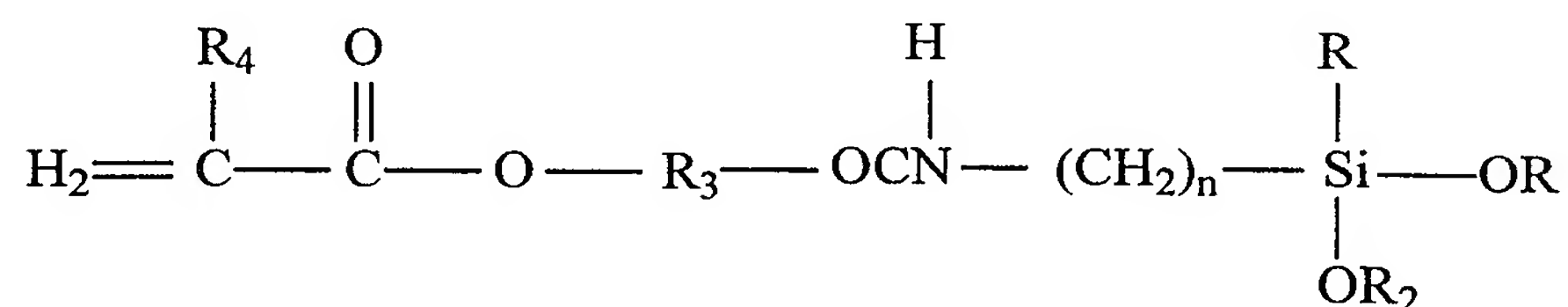
Consistent with the aforescribed components of the silane polymer,
20 one particular example of a silane polymer useful in the coating composition of this invention may contain the following constituents: about 15 to 25% by weight styrene, about 30 to 60% by weight methacryloxypropyltrimethoxy silane, and about 25 to 50% by weight trimethylcyclohexyl methacrylate.

One preferred silane polymer contains about 30% by weight styrene,
25 about 50% by weight methacryloxypropyl trimethoxy silane, and about 20% by weight of nonfunctional acrylates or methacrylates such as trimethylcyclohexyl methacrylate, butyl acrylate, and iso-butyl methacrylate and any mixtures thereof.

Silane functional macromonomers also can be used in forming the silane polymer. These macromonomers are the reaction product of a silane
30 containing compound, having a reactive group such as epoxide or isocyanate, with an ethylenically unsaturated non-silane containing monomer having a reactive group, typically a hydroxyl or an epoxide group, that is co-reactive with the silane monomer. An example of a useful macromonomer is the reaction product of a hydroxy functional ethylenically unsaturated monomer such as a hydroxyalkyl

acrylate or methacrylate having 1 to 4, preferably 2 to 3 carbon atoms in the alkyl group and an isocyanatoalkyl alkoxysilane such as isocyanatopropyl triethoxysilane.

Typical of such above-mentioned silane functional macromonomers are those having the following structural formula:



wherein R, R₁, and R₂ are as described above; R₄ is H or CH₃, R₃ is an alkylene group having 1 to 8, preferably 1 to 4 carbon atoms and n is a positive integer from 1 to 8, preferably from 1 to 4.

The coating composition of the present invention, which is formulated into high solids coating systems further contains at least one organic solvent typically selected from the group consisting of aromatic hydrocarbons such as petroleum naphtha or xylenes; ketones such as methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; esters such as butyl acetate or hexyl acetate; and glycol ether esters, such as propylene glycol monomethyl ether acetate. The amount of organic solvent added depends upon the desired solids level as well as the desired amount of VOC of the composition. If desired, the organic solvent may be added to both components of the binder.

The coating composition of the present invention may also contain conventional additives such as stabilizers, and rheology control agents, flow agents, and toughening agents. Such additional additives will, of course, depend on the intended use of the coating composition. Any additives that would adversely effect the clarity of the cured coating will not be included as the composition is used as a clear coating. The foregoing additives may be added to either component or both, depending upon the intended use of the coating composition.

The clear coating composition of the present invention may be supplied in the form of a two-pack coating composition in which the first-pack includes the polyisocyanate component and the second-pack includes the melamine component. Generally the first and the second pack are stored in separate containers and mixed before use. The containers are preferably sealed air tight to prevent degradation during storage. The mixing may be done, for example, in a mixing nozzle or in a container.

Alternatively, when the isocyanate functionalities of the polyisocyanate are blocked, both the components of the coating composition can be stored in the same container in the form of a one-pack coating composition.

To improve weatherability of the clear finish of the coating composition, about 0.1 to 5%, by weight, based on the weight of the composition solids, of an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers and absorbers may be added. These stabilizers include ultraviolet light absorbers, screeners, quenchers and specific hindered amine light stabilizers. Also, about 0.1 to 5% by weight, based on the weight of the composition solids, of an antioxidant can be added. Typical ultraviolet light stabilizers that are useful include benzophenones, such as hydroxydodecylbenzo-phenone, 2,4-dihydroxybenzophenone; triazoles, such as 2-phenyl-4-(2'-4'-dihydroxybenzoyl)triazoles; and triazines, such as 3,5-dialkyl-4-hydroxyphenyl derivatives of triazine and triazoles such as 2-(benzotriazole-2-yl)-4,6-bis(methylethyl-1-phenyl ethyl)phenol, 2-(3-hydroxy-3,5'-di-tert amyl phenyl) benzotriazole, 2-(3',5'-bis(1,1-dimethylpropyl)-2'-hydroxyphenyl)-2H-benzotriazole, benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-C₇₋₉-branched alkyl esters, and 2-(3',5'-bis(1-methyl-1-phenylethyl)-2'-hydroxyphenyl)benzotriazole.

Typical hindered amine light stabilizers are bis(2,2,6,6-tetramethylpiperidynyl)sebacate, bis(N-methyl-2,2,6,6-tetramethylpiperidynyl)sebacate and bis(N-octyloxy-2,2,6,6-tetramethylpiperidynyl)sebacate. One of the useful blends of ultraviolet light absorbers and hindered amine light stabilizers is bis(N-octyloxy-2,2,6,6-tetramethylpiperidynyl)sebacate and benzenepropanoic acid, 3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxy-, C₇₋₉-branched alkyl esters. Another useful blend of ultraviolet light absorbers and hindered amine light stabilizers is 2-(3',5'-bis(1-methyl-1-phenylethyl)-2'-hydroxyphenyl)benzotriazole and decanedioic acid, bis(2,2,6,6-tetramethyl-4-piperidynyl)ester both supplied by Ciba Specialty Chemicals, Tarrytown, New York under the trademark Tinuvin[®] 900 and Tinuvin[®] 123, respectively.

The coating composition of the present invention optionally contains in the range of from 0.1 percent to 40 percent, preferably in the range of from 5 percent to 35 percent, and more preferably in the range of from 10 percent to 30 percent of a flow modifying resin, such as a non-aqueous dispersion (NAD), all percentages being based on the total weight of composition solids. The weight average molecular weight of the flow modifying resin generally varies in the

range of from 20,000 to 100,000, preferably in the range of from 25,000 to 80,000 and more preferably in the range from 30,000 to 50,000.

The non-aqueous dispersion-type resin is prepared by dispersion-polymerizing at least one vinyl monomer in the presence of a polymer dispersion stabilizer and an organic solvent. The polymer dispersion stabilizer may be any of the known stabilizers used commonly in the field of non-aqueous dispersions, and may include the following substances (1) through (9) as examples:

(1) A polyester macromer having about 1.0 polymerizable double bond within the molecule as obtainable upon addition of glycidyl acrylate or glycidyl methacrylate to an auto-condensation polyester of a hydroxy-containing fatty acid such as 12-hydroxystearic acid.

(2) A comb-type polymer prepared by copolymerizing the polyester macromer mentioned under (1) with methyl methacrylate and/or other (meth)acrylic ester or a vinyl monomer.

(3) A polymer obtainable by the steps of copolymerizing the polymer described under (2) with a small amount of glycidyl (meth)acrylate and, then, adding (meth)acrylic acid to the glycidyl groups thereof so as to introduce double bonds.

(4) A hydroxy-containing acrylic copolymer prepared by copolymerizing at least 20 percent by weight of (meth)acrylic ester of a monohydric alcohol containing 4 or more carbon atoms.

(5) An acrylic copolymer obtainable by producing at least 0.3 double bond per molecule based on its number average molecular weight, into the copolymer mentioned under (4). A method for introducing double bonds may, for example, comprise copolymerizing the acrylic polymer with a small amount of glycidyl (meth)acrylate and then adding (meth)acrylic acid to the glycidyl group.

(6) An alkylmelamine resin with a high tolerance to mineral spirit.

(7) An alkyd resin with an oil length not less than 15 percent and/or a resin obtainable by introducing polymerizable double bonds into the alkyd resin. A method of introducing double bonds may, for example, comprise addition reaction of glycidyl (meth)acrylate to the carboxyl groups in the alkyd resin.

(8) An oil-free polyester resin with a high tolerance to mineral spirit, an alkyd resin with an oil length less than 15 percent, and/or a resin obtainable by introducing double bonds into said alkyd resin.

(9) A cellulose acetate butyrate into which polymerizable double bonds have been introduced. An exemplary method of introducing double bonds comprises addition reaction of isocyanatoethyl methacrylate to cellulose acetate butyrate.

These dispersion stabilizers can be used alone or in combination.

Among the aforementioned dispersion stabilizers, preferred for the purposes of the invention are those which can be dissolved in comparatively low polar solvents, such as aliphatic hydrocarbons to assure the film performance requirements to some extent. As dispersion stabilizers which can meet such conditions, the acrylic copolymers mentioned under (4) and (5) are desirable in that they not only lend themselves well to adjustment of molecular weight, glass transition temperature, polarity (polymer SP value), hydroxyl value, acid value and other parameters but are excellent in weatherability. More desirable are acrylic copolymers containing an average of about 0.2 to about 1.2 polymerizable double bonds, per molecule, which are graft copolymerized with dispersed particles.

The non-aqueous dispersion-type resin used in accordance with this invention can be easily prepared by dispersion-polymerizing at least one vinyl monomer in the presence of the aforescribed polymer dispersion stabilizer and an organic solvent, which mainly contains an aliphatic hydrocarbon. The dispersion stabilizer and the vinyl monomer are soluble in the organic solvent. However, the polymer particles formed by the vinyl monomer are not soluble in the solvent.

The monomer component forming the acrylic copolymer suitable as the polymer dispersion stabilizer and the vinyl monomer forming the dispersed particles may be virtually any radical-polymerizable unsaturated monomer. A variety of monomers can be utilized for the purpose. Typical examples of such monomers include the following.

(a) Esters of acrylic acid or methacrylic acid, such as for example, C₁₋₁₈ alkyl esters of acrylic or methacrylic acid, such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, stearyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate, lauryl methacrylate, and stearyl methacrylate; glycidyl acrylate and glycidyl methacrylate; C₂₋₈ alkenyl esters of acrylic or methacrylic acid, such as allyl acrylate, and allyl methacrylate; C₂₋₈ hydroxyalkyl esters of acrylic or methacrylic acid, such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, and hydroxypropyl methacrylate; and C₃₋₁₈ alkenyloxyalkyl esters of acrylic or methacrylic acid, such as allyloxyethyl acrylate, and allyloxyethyl methacrylate.

(b) Vinyl aromatic compounds, such as, for example, styrene, α -methylstyrene, vinyltoluene, p-chlorostyrene, and vinylpyridine.

(c) α , β -Ethylenically unsaturated acids, such as, for example, acrylic acid, methacrylic acid, itaconic acid and crotonic acid

(d) Amides of acrylic or methacrylic acid, such as, for example, acrylamide, methacrylamide, n-butoxymethylacrylamide, N-methylolacrylamide, 5 n-butoxymethylmethacrylamide, and N-methylolmethacrylamide.

(e) Others: for example, acrylonitrile, methacrylonitrile, methyl isopropenyl ketone, vinyl acetate, VeoVa monomer (product of Shell Chemicals, Co., Ltd.; mixed vinyl esters of a synthetic saturated monocarboxylic acid of highly branched structure containing ten carbon atoms), vinyl propionate, vinyl 10 pivalate, isocyanatoethyl methacrylate, perfluorocyclohexyl (meth)acrylate, p-styrenesulfonamide, N-methyl-p-styrenesulfonamide, and γ -methacryloyloxypropyl trimethoxy silane.

Among the monomers mentioned above, the following materials can be used with particular advantage for the preparation of the acrylic copolymer 15 used as a dispersion stabilizer:

Mixed monomers based on comparatively long-chain, low-polar monomers, such as n-butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, lauryl methacrylate, and stearyl methacrylate, supplemented as necessary with styrene, methyl (meth)acrylate, ethyl (meth)acrylate, 2- 20 hydroxyethyl (meth)acrylate, propyl (meth)acrylate, and (meth)acrylic acid. The dispersion stabilizer may be one prepared by adding glycidyl (meth)acrylate or isocyanatoethyl methacrylate to a copolymer of the monomers for introduction of polymerizable double bonds.

The acrylic copolymer used as the dispersion stabilizer can be easily 25 prepared using a radical polymerization initiator in accordance with the known solution polymerization process.

The number average molecular weight of the dispersion stabilizer is preferably in the range of about 1,000 to about 50,000 and, for still better results, about 3,000 to about 20,000.

30 Among the monomers mentioned above, particularly preferred vinyl monomers for the formation of the dispersed polymer particles predominantly contain comparatively high-polarity monomers, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, and acrylonitrile, supplemented as necessary with (meth)-acrylic acid, and 2-hydroxyethyl (meth)acrylate. It is also 35 possible to provide gel particles as cross-linked in molecules by copolymerizing a small amount of polyfunctional monomers, such as divinylbenzene, and ethylene glycol dimethacrylate, by copolymerizing a plurality of monomers having mutually reactive functional groups, such as glycidyl methacrylate and

methacrylic acid, or by copolymerizing an auto-reactive monomer, such as N-alkoxymethylated acrylamides, and γ -methacryloyloxypropyl trimethoxy silanes.

In conducting the dispersion polymerization, the ratio of the dispersion stabilizer to the vinyl monomer forming dispersed particles is selected from the range of about 5/95 to about 80/20 by weight, preferably about 10/90 to about 60/40 by weight, and the dispersion polymerization can be conducted in the presence of a radical polymerization initiator by a known procedure.

While the particle size of the resulting non-aqueous dispersion type acrylic resin is generally in the range of about 0.05 μm to about 2 μm , the range of about 0.1 μm to about 0.7 μm is preferable from the stability of shelf life and the gloss, smoothness and weatherability of the film.

In use, the first-pack of the two-pack coating composition containing the polyisocyanate and the second-pack containing the melamine and silane component are mixed just prior to use or about 5 to 30 minutes before use to form a pot mix, which has limited pot life of about 10 minutes to about 6 hours. Thereafter, it becomes too viscous to permit application through conventional application systems, such as spraying. A layer of the pot mix is typically applied to a substrate by conventional techniques, such as spraying, electrostatic spraying, roller coating, dipping or brushing. Generally, a clear coat layer having a thickness in the range of from 25 micrometers to 75 micrometers is applied over a metal substrate, such as automotive body, which is often pre-coated with other coating layers, such as an electrocoat, primer and a basecoat. The two pack coating composition may be baked upon application for about 60 to 10 minutes at about 80°C to 160°C.

When the one-pack coating composition containing the blocked polyisocyanate is used, a layer thereof applied over a substrate using aforescribed application techniques, is cured at a baking temperature in the range of from 80°C to 200°C, preferably in the range of 80°C to 160°C, for about 60 to 10 minutes. It is understood that actual baking temperature would vary depending upon the catalyst and the amount thereof, thickness of the layer being cured and the blocked isocyanate functionalities and the melamine utilized in the coating composition. The use of the foregoing baking step is particularly useful under OEM (Original Equipment Manufacture) conditions.

The clear coating composition of the present invention is suitable for providing clear coatings on variety of substrates, such as metal, wood and concrete substrates. The present composition is especially suitable for providing clear coatings in automotive OEM or refinish applications. These compositions

are also suitable as clear coatings in industrial and maintenance coating applications.

The invention is illustrated in the following Examples:

EXAMPLES

5

Blocked Isocyanurate 1

A mixture of 500 parts of methyl amyl ketone, 1211 parts of 2 ethyl hexanol and 0.3 part of dibutyl tin dilaurate was heated to 60°C under nitrogen blanket in a flask fitted with a mixer and a condenser. Then 1796 parts of isocyanurate of hexane diisocyanate (Desmodur[®] 3300 by Bayer Corporation) were added to the reaction mixture, which resulted in an exothermic reaction. The exothermal reaction was controlled by maintaining the reaction temperature at or below 100°C. Then 45 parts of methyl amyl ketone were added. The reaction mixture was held at 90°C for 1 hour to yield 2 ethyl hexanol blocked isocyanurate of hexane diisocyanate.

15

Blocked Isocyanurate 2

A mixture of 1044 parts of methyl amyl ketone, 1746 parts of isocyanurate of hexane diisocyanate (Desmodur[®]3300 supplied by Bayer Corporation, Pittsburgh, Pennsylvania), and 0.3 part of dibutyl tin dilaurate was heated to 80 °C under nitrogen blanket in a flask fitted with a mixer and a condenser. Then 902 parts of cyclohexanol were added to the reaction mixture over a period of 20 minutes, followed by the addition of 45 parts of methyl amyl ketone. The reaction mixture was held at 100°C for 1.5 hour to yield cyclohexanol blocked isocyanurate of hexane diisocyanate.

25

Silane Polymer 1

In a flask fitted with a mixer and a condenser, 158 parts of aliphatic solvent were heated to reflux. A mixture of 140 parts of styrene, 140 parts of isobornyl methacrylate, 304 parts of methacryloxypropyltrimethoxysilane (UCARSIL[®]A-174 by Witco), 82 parts of aliphatic solvent and 16 parts of tertiary butyl peracetate were added over a period of 240 minutes. The reaction mixture was held for 1 hour to yield a polymer containing methacryloxypropyltrimethoxysilane.

30

Silane Polymer 2 (Silane functional Polyurethane Polymer)

To a 5 liter reactor fitted with heating mantle, stirrer, and under nitrogen blanket, 1035.7 parts of Aromatic 100 solvent, 206.48 parts of propylene carbonate (supplied by Huntsman Corporation, Austin, Texas), and 340.2 parts aminopropyl trimethoxy silane (supplied by OSI Corporation, Tarrytown, New York) were charged. The reaction mixture was heated under agitation to 120°C, held 4 hours and then cooled to 100°C. A shot of 570.49 parts of cyclohexanol (supplied by Aldrich Chemical Company, Milwaukee, Wisconsin), 40 parts of Aromatic 100 solvent, and 0.3 parts of dibutyltin dilaurate catalyst (supplied by Air Products, Allentown, Pennsylvania) was added. Thereafter, a polyisocyanate solution of 1472.7 parts of Desmodur[®] 3300 polyisocyanate (supplied by Bayer Corporation, Pittsburgh, Pennsylvania) with 240 parts Aromatic 100 solvent. The rate of addition was adjusted to control the resulting exothermic reaction by maintaining the reaction temperature at 120°C. The reaction mixture was held at 120°C for 3.8 hours at which point the isocyanate had been completely consumed as determined by the absence of the isocyanate absorbance at 2220 cm^{-1} in the infrared spectrum. The resulting silane polymer had viscosity of 12,300 cps at 70.52% nv. It should be noted that absent the silane functionality the polymer would have viscosity three times the viscosity of the aforescribed silane polymer.

The aforescribed components along with the additional components described in Table 1 below were used to prepare clearcoat compositions of Example 1 of the present invention and Comparative Examples 1 and 2.

Table 1: Clearcoat Compositions

	Comparative Example 1	Comparative Example 2	Example 1
Monomeric melamine ¹	32	32	32
Blocked Isocyanurate 1		58	37
Blocked Isocyanurate 2	60		
Silane Polymer 1			28
NAD ²	46	46	31
HALS Tinuvin [®] 123 ³	2	2	2
UVA Tinuvin [®] 1130 ⁴	2	2	2
Catalyst 1 ⁵	4.5	4.5	3.5
Catalyst 2 ⁶			0.1

1 Cymel® 1168 (methylated butylated melamine from Cytec Industries Inc., West Patterson, New York

2 Prepared in accordance with the US Patent 5,747,590 at column 8, lines 46-68 and column 9, lines 1-25, all of which is incorporated herein by reference

3 Supplied by Ciba Specialty Chemicals, Tarrytown, New York

4. Supplied by Ciba Specialty Chemicals, Tarrytown, New York

5 Phenyl acid phosphate salt of 2-amino-2 methyl-1-propanol supplied by King Industries, Norwalk, Connecticut

6 Dibutyl tin dilaurate supplied by Air Product, Allentown, Pennsylvania

Layers from clearcoat compositions from Example 1 and

Comparative Examples 1 and 2 were spray applied wet-on-wet over a basecoat on a primed phosphated steel panels and then bake cured for 30 minutes at 140°C to form coatings thereon. Applicants unexpected discovery of the dramatic improvement in the coating properties when the aforescribed Silane Polymer 1 is added to the melamine/isocyanate components can be seen from the coating properties of Example 1 and Comparative Examples 1 and 2 measured and reported in Table 2 below:

Table 2: Properties

Properties	Test Method	Comparative Example 1	Comparative Example 2	Example 1
Dry film thickness	ASTM D1400	32 microns	32 microns	32 microns
20° Gloss	ASTMD523	84	84	94
DOI	ASTM D5767	83	80.2	92.3
Tukon Hardness	ASTM D1474	6.2	14.1	14.1
% Retention dry mar	ASTM D5178	80	92	98
% Retention wet mar	ASTM D5178	92	81	86
Acid etch	Jacksonville, Florida exposure for 3 months ¹	8.33	6.17	5.5

¹ On a scale of 1 to 10 (1 being the best and 10 being the worst).

5 From the data reported in Table 2 it is readily apparent that the presence of silane polymer in the clearcoat composition substantially improves the appearance of the coating with substantially comparable or better acid etch and mar resistances and film hardness.

What is claimed is:

1. A clear coating composition comprising isocyanate, silane and melamine components wherein said isocyanate component comprises an aliphatic polyisocyanate having on an average 2 to 6 isocyanate functionalities.
- 5 2. The composition of claim 1 wherein said isocyanate functionalities are blocked by reacting said functionalities with a monomeric alcohol.
3. The composition of claim 2 wherein said monomeric alcohol is an aliphatic alcohol.
4. The composition of claim 1 wherein said silane component
10 comprises at least one silane polymer having one or more reactive silane group.
5. The composition of claim 1 or 2 wherein said composition further comprises one or more organo tin or acid catalysts.
6. The composition of claim 5 wherein said organo tin catalyst is selected from the group consisting of dibutyl tin diacetate, dibutyl tin dilaurate,
15 stannous octate, and a combination thereof.
7. The composition of claim 5 wherein the acid catalyst is selected from the group consisting of dodecylbenzene sulfonic acid, dodecylbenzene sulfonic acid blocked with an amine, para-toluenesulfonic acid, para-toluenesulfonic acid blocked with an amine, phenyl acid phosphate, phenyl acid
20 phosphate blocked with an amine dinonylnaphthalene sulfonic acid, dinonylnaphthalene sulfonic acid blocked with an amine and a combination thereof.
8. The composition of claim 7 wherein said amine is dimethyl oxazolidine, 2-amino-2-methyl-1-propanol, n,n-dimethylethanolamine or a
25 combination thereof.
9. The composition of claim 5, 6 or 7 wherein said composition comprises in the range of from 0.001 percent to 5.0 percent of said catalyst, all percentages being weight percentages based on the total weight of composition solids.
- 30 10. The composition of claim 1 wherein said polyisocyanate comprises one or more trimers of hexamethylene diisocyanate, isophorone diisocyanate, meta-tetramethylxylylene diisocyanate, or a combination thereof.
11. The composition of claim 1 or 6 comprises in the range of from 35 percent to 70 percent said polyisocyanate wherein all percentages are in weight
35 based on the total weight of composition solids.
12. The composition of claim 1, 2 or 10 wherein said polyisocyanate has an average 2.5 to 6 isocyanate functionalities.

13. The composition of claim 1 wherein said melamine component comprises a monomeric melamine, a polymeric melamine, or a combination thereof.

14. The composition of claim 1 or 13 comprises in the range of from 10 percent to 40 percent of said melamine component wherein all percentages are in weight based on the total weight of composition solids.

15. The composition of claim 1 further comprises a flow modifying resin.

16. The composition of claim 1 comprises in the range of from 5 percent to 45 percent of said silane component, all percentages being in weight percentages based on the total weight of composition solids.

17. The composition of claim 1 in the form of a two-pack composition wherein a first-pack of said two-pack composition comprises said polyisocyanate component and a second-pack of said two-pack composition comprises said melamine and silane components.

18. The composition of claim 1 wherein a VOC of said composition varies in the range of from 0.0 to 0.472 kilogram of an organic solvent per liter of the composition.

19. The clear coating composition of claim 1 wherein a clear coating on a substrate produced from said composition has a DOI rating of at least 80.

20. The composition of claim 1 further comprises ultra violet light stabilizers, light absorbers or a combination thereof.

21. A method of producing a clear coating on a substrate comprising: applying a layer of a clear coating composition comprising isocyanate, silane and melamine components wherein said isocyanate component comprises an aliphatic polyisocyanate having on an average 2 to 6 isocyanate functionalities; and curing said layer into said clear coating.

22. The method of claim 21 wherein said coating has a DOI rating of at least 80.

23. The method of claim 21 wherein said coating has a 20° gloss of at least 80.

24. The method of claim 21 wherein said isocyanate functionalities of the polyisocyanate are blocked by reacting said polyisocyanate with a monomeric alcohol.

25. The method of claim 24 wherein said monomeric alcohol is cyclohexanol, 2-ethyl hexanol or a mixture thereof.

26. The method of claim 24 or 25 wherein said curing of said layer takes place at an elevated baking temperature in the range 80°C to 160°C.

27. The method of claim 21 wherein said composition comprises in the range of from 5 percent to 45 percent of said silane component, all percentages being in weight percentages based on the total weight of composition solids.

5

RECTIFIED SHEET (RULE 91)
ISA/EP

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/06963

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G18/28 C09D175/04 C08G18/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 34905 A (PPG INDUSTRIES) 7 November 1996 (1996-11-07) page 10, line 5 -page 11, line 4 page 12, line 4 -page 16, line 3 page 18, line 14 - line 21 page 23, line 18 - line 30; claims 1,20,24; example 4 ----	1,4
X	EP 0 017 187 A (BAYER) 15 October 1980 (1980-10-15) page 4, line 5 -page 5, line 20; examples page 7, line 18 -page 10, line 1 page 19; claim 1 ---- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

25 July 2000

Date of mailing of the international search report

03/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bourgonje, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/06963

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	W0 99 19411 A (E.I. DU PONT DE NEMOURS) 22 April 1999 (1999-04-22) page 3, line 15 -page 6, line 20 page 10, line 14 - line 35 page 19, line 8 - line 24 ---	1,4
X	W0 96 25466 A (E. I. DU PONT DE NEMOURS) 22 August 1996 (1996-08-22) page 3, line 1 -page 5, line 5 page 7, line 29 -page 8, line 5 page 9, line 11 - line 22 ---	1,4
A	W0 97 22647 A (E.I.DU PONT DE NEMOURS) 26 June 1997 (1997-06-26) page 3, line 3 -page 7, line 19 page 8, line 23 - line 26 ---	1,4
A	EP 0 708 159 A (BASF) 24 April 1996 (1996-04-24) the whole document ---	1
A	DATABASE WPI Week 9346 Derwent Publications Ltd., London, GB; AN 365463 XP002143388 "Coating composition for cars" & JP 05 271608 A (KANSAI PAINT), 19 October 1993 (1993-10-19) abstract -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/06963

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9634905 A	07-11-1996	AU 5633296 A CA 2207928 A EP 0823922 A JP 3017539 B JP 11500174 T US 5891981 A	21-11-1996 07-11-1996 18-02-1998 13-03-2000 06-01-1999 06-04-1999
EP 17187 A	15-10-1980	DE 2914427 A CA 1165492 A DE 3060959 D JP 1419218 C JP 55139466 A JP 62023991 B US 4315091 A	23-10-1980 10-04-1984 25-11-1982 14-01-1988 31-10-1980 26-05-1987 09-02-1982
WO 9919411 A	22-04-1999	AU 9694198 A	03-05-1999
WO 9625466 A	22-08-1996	CA 2212667 A EP 0809678 A JP 11500168 T	22-08-1996 03-12-1997 06-01-1999
WO 9722647 A	26-06-1997	US 5684084 A AU 709839 B AU 1467697 A CA 2240534 A EP 0868460 A JP 2000503047 T	04-11-1997 09-09-1999 14-07-1997 26-06-1997 07-10-1998 14-03-2000
EP 708159 A	24-04-1996	BR 9504425 A CA 2160654 A JP 8188746 A	20-05-1997 18-04-1996 23-07-1996
JP 5271608 A	19-10-1993	NONE	